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**Semiannual Progress Report
June-December 1976**

Submitted to

National Aeronautics and Space Administration

**(NASA-CR-164151) RESEARCH IN ACETYLENE
CONTAINING MONOMERS Semiannual Progress
Report, Jun. - Dec. 1976 (Virginia
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NASA Grant No: NSG 1286

Title of Grant: Research in Acetylene Containing Monomers

Principal Investigator:

**Michael A. Ogliaruso
Department of Chemistry
Virginia Polytechnic Institute
and State University
Blacksburg, Virginia 24061**



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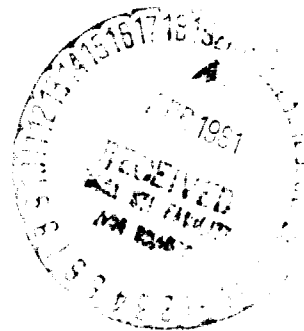
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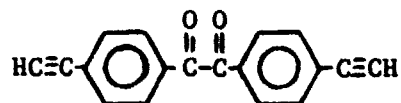
Purpose

The purpose of this research is to prepare precursor bisbenzils with pendant acetylene linkages to be used in the synthesis of new aromatic poly(phenylquinoxalines) (PPQ).

Detailed Research Approach

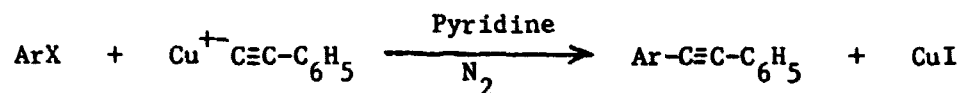
The initial research approach used is described on the following pages of this report.

Our initial attempt to prepare I was based upon the findings of



I

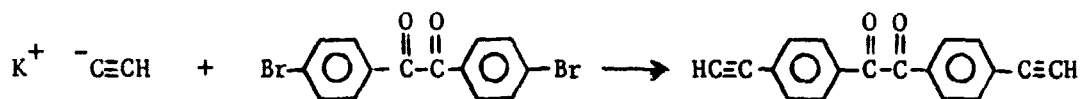
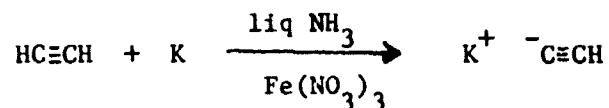
Castro, et al.¹ that the interaction of aryl halides and cuprous acetylides gives rise to tolans.



Private communication with Prof. Castro revealed that although the cuprous acetylides gave good yields in this reaction they are extremely dangerous starting materials and that slightly lower yields of product could be obtained by using solutions of sodium acetylide in liquid ammonia which are not dangerous. In view of this information and the findings of Wentworth and Mulligan² that dihalides can react with two moles of cuprous acetylides to give bis-tolans, our initial attempt at a model reaction for

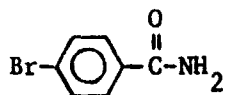


the preparation of I consisted of the following reaction sequence:

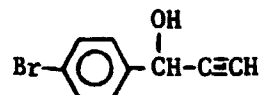


I

Only two organic products were isolated from this reaction, neither of which was the desired product I. The products isolated were p-bromobenzamide (II), and 3-(p-bromophenyl)-3-hydroxypropyne (III) in 50 and 30% yields respectively.



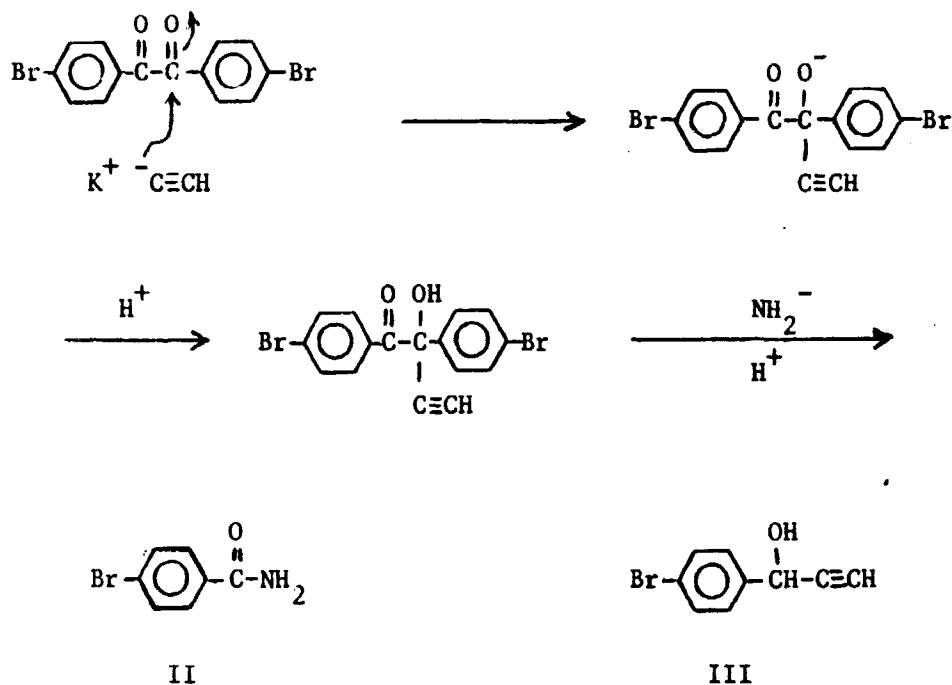
II



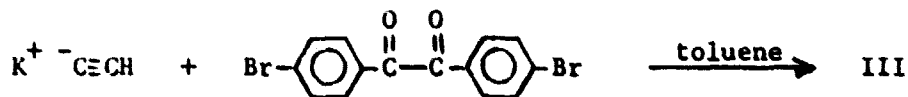
III

Also isolated was 10% of a yellow oil which could not be crystallized, but which showed both a carbonyl (by ir) and a halide (by Beilstein test) to be present.

Both major products can be seen to occur from attack of the potassium acetylide on one of the benzil carbonyl groups followed by cleavage:



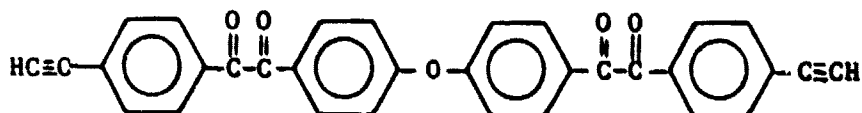
To avoid this problem the reaction was attempted using toluene as the solvent to prepare the potassium acetylide. This reaction gave a 75% yield of III and a 15% yield of the same yellow oil referred to above.



A thorough review of the literature brought to light a publication³ by Cymerman-Craig and co-workers in which they reported the extensive investigation they conducted on the reaction of sodium acetylide with benzil and related compounds. They investigated the reaction of benzil with sodium acetylide in liquid ammonia and ether, and the reaction of benzil with potassium acetylide in *t*-amyl alcohol. In all cases benzamide or 3-phenyl-3-hydroxypropyne were the major products, indicating attack of the nucleophile on one of the carbonyl carbons followed by cleavage of the carbonyl carbon to carbon bond.

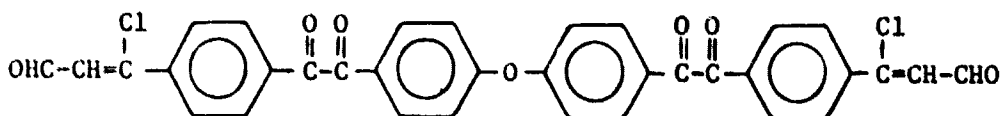
In order to avoid the presence of sodium amide which cleaves the carbonyl carbon to carbon bond, we attempted to prepare a finely dispersed mixture of potassium in toluene. This preparation called for the addition of small pieces of potassium to refluxing toluene, mixed by means of a high speed stirrer. Upon addition of potassium to the hot, stirred toluene solution an explosion resulted, which fortunately was not serious, but which precluded our further use of this approach.

At this point a decision was made to investigate the Vilsmeier reaction as a method of preparing (4-(*p*-phenylacetylene)glyoxalylphenyl ether (IV).



IV

By the work of Hergenrother, et al⁴ it was known that treatment of the intermediate 4-(β-chlorovinylcinnamaldehyde)glyoxalylphenyl ether (V) with base to effect cleavage of the β-chlorovinyl aldehyde function and thus produce the acetylene function, gave rise to cleavage of the

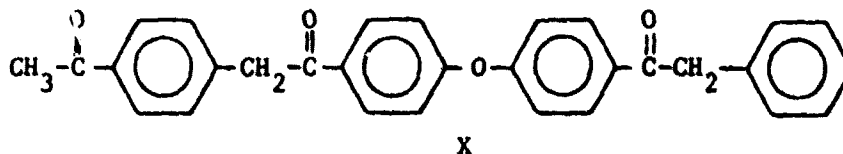


V

carbonyl carbon to carbon bond. To avoid this possibility it was decided to attempt the Vilsmeier reaction on the 4-(p-acetylphenyl)acetylphenyl ether with the hope that the terminal acetylene function could be introduced without cleavage of the molecule, and then oxidation to the diketone could be accomplished. An outline of this approach appears in Scheme 1.

The procedure for the preparation of 4-phenylacetylphenyl ether (VI) was essentially the one already published⁵ and afforded the product in 77% yield. Conversion of VI to VII was accomplished in 78% yield. It was noted at this point that if one mole of acetyl chloride was allowed

to react with one mole of VI, a monoacetylated product X could be obtained in 52% yield.

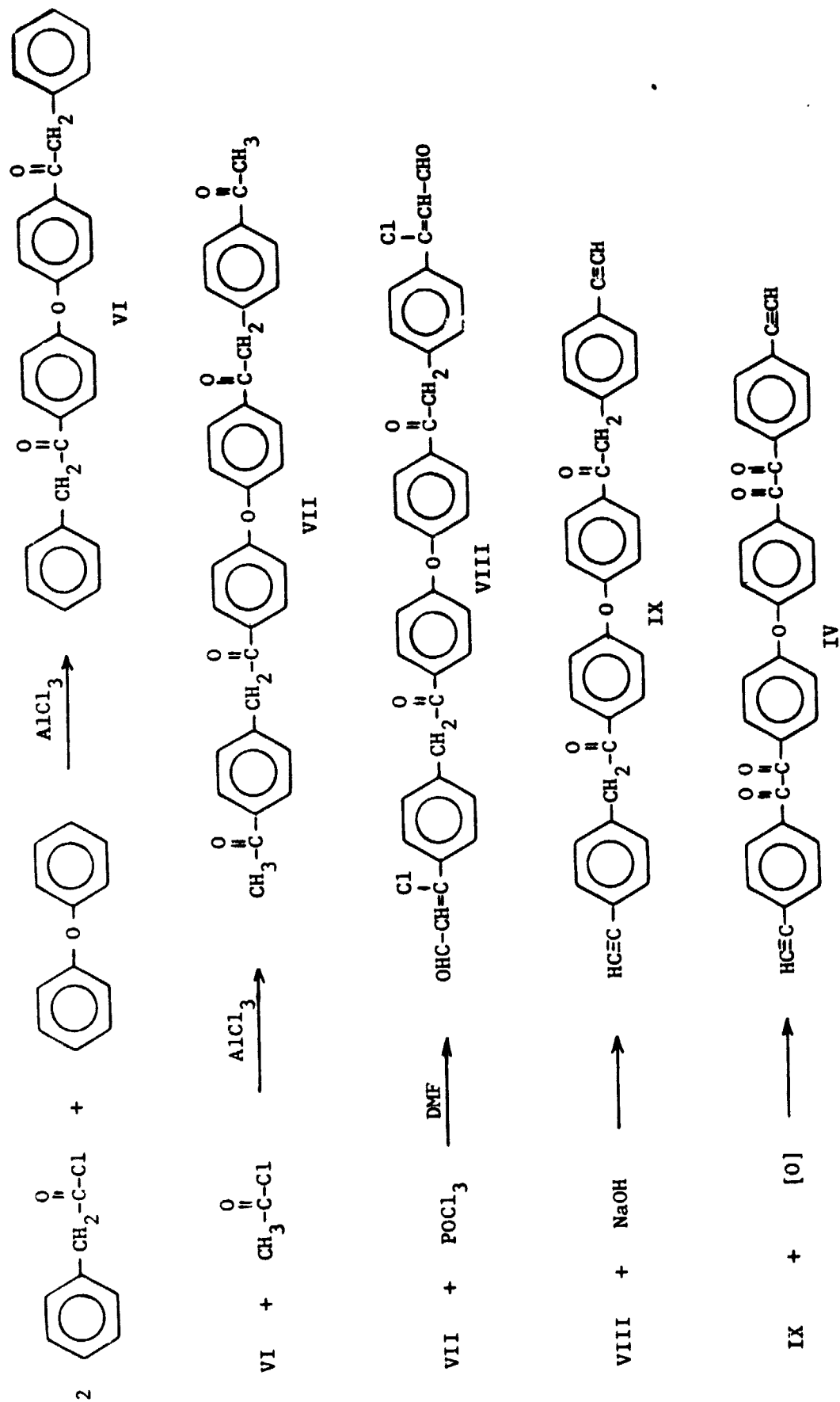


At this point the reaction between VI and the Vilsmeier reagent was investigated to see if the activated methylene group would react with the Vilsmeier reagent. This reaction was attempted using a 1:10 mole ratio of VI to Vilsmeier reagent, and a 99.4% yield of 4-(β -chlorovinylcinnamaldehyde)phenyl ether was obtained (Scheme 2).

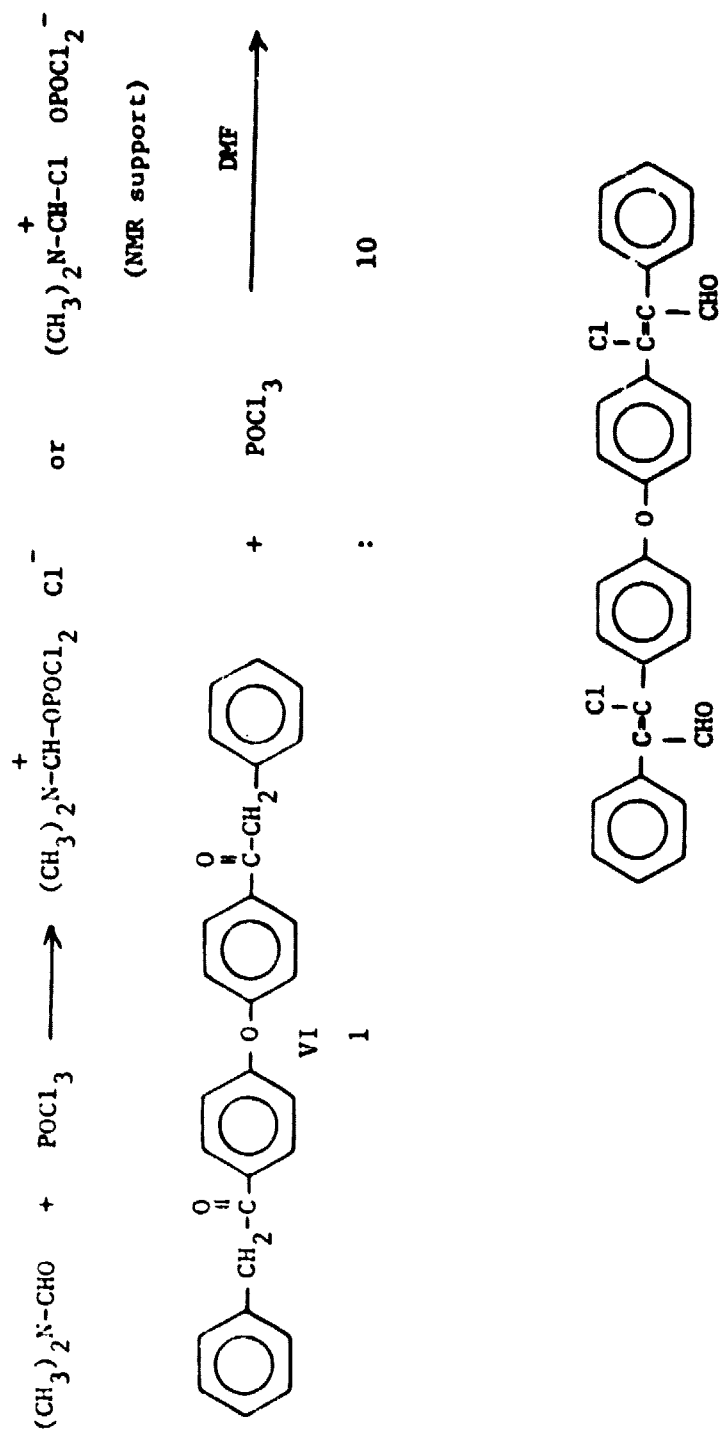
It was then felt that reaction of VII with the Vilsmeier reagent might afford the desired product by preferential reaction of the acetyl groups with the Vilsmeier reagent, leaving the methylene groups in-tact. To test this hypothesis, varying ratios of VII to Vilsmeier reagent were allowed to react and in all cases only one methylene group was seen to remain unattacked (Scheme 3).

The same reaction was run on the monoacetylated phenylacetylphenyl ether (XI), but again only one methylene group was seen to remain unattacked (Scheme 4). At this point this approach was abandoned and a new approach was attempted.

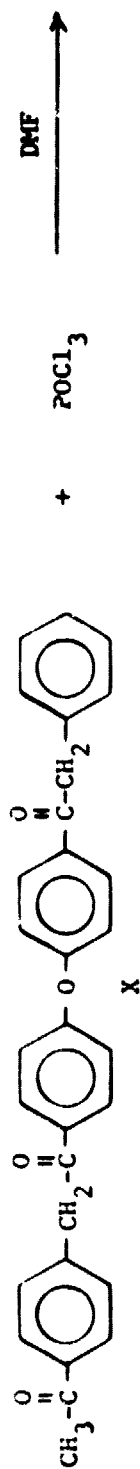
Scheme 1



Scheme 2

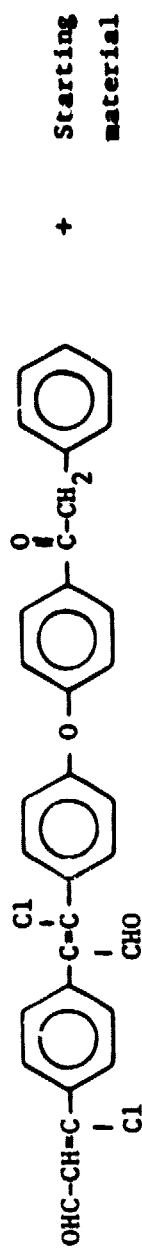


Scheme 4



1 : 3

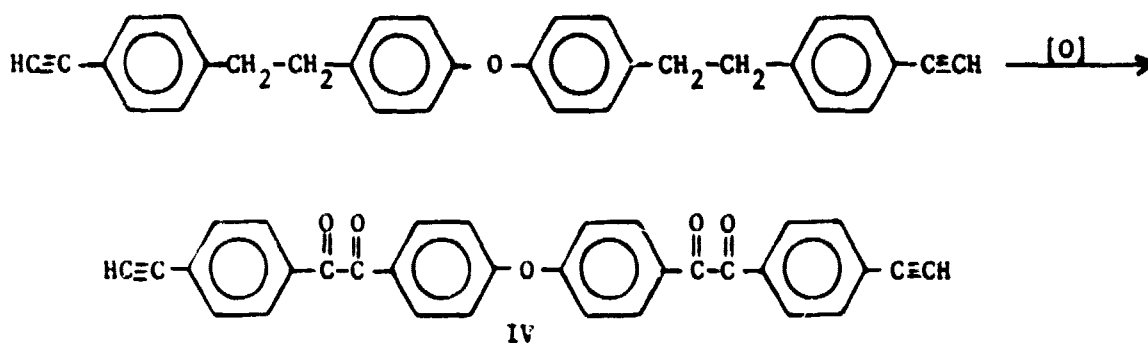
1 : 1.2



1 : 3 ratio gave 50%

1 : 1.2 ratio gave 10%

Since it had proved difficult to introduce the terminal acetylene linkage into either the 4-phenylacetylphenyl ether of the bis-benzil without destroying some other functional group in the molecules by either the sodium acetylide or the Vilsmeier routes, it was decided to attempt introduction of the terminal acetylene function into 4-phenethylphenyl ether and oxidize the ethyl functions to benzils.



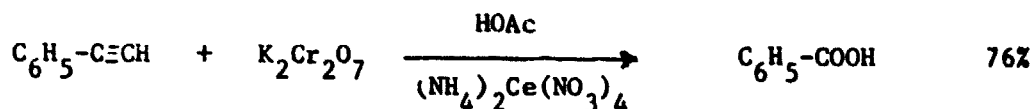
In order to try this approach an oxidizing agent was sought which would convert bibenzil (XI) into benzil, and it was found that potassium dichromate in acetic acid catalyzed by ceric ammonium nitrate would oxidize the two methylene functions into a diketone. A study of the conditions and amounts of reagents was made to find the best yield of product. The results of this study are shown in Table I, where the percent yield in brackets is the yield obtained by taking into account the recovered starting bibenzil.

Since it was found possible to convert the two methylene functions into a diketone, the next step was to investigate if this oxidizing agent mixture would cleave the terminal triple bond which would be present in

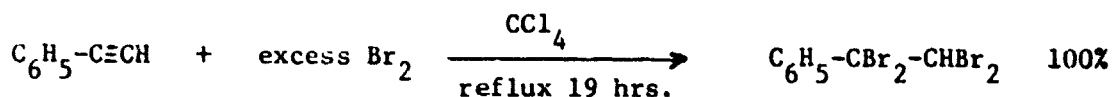
Table I

| $\text{C}_6\text{H}_5\text{-CH}_2\text{-CH}_2\text{-C}_6\text{H}_5 + \text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow[\text{(NH}_4)_2\text{Ce(NO}_3)_4]{\text{HOAc}} \text{C}_6\text{H}_5\text{-CO-CO-C}_6\text{H}_5$ | | | | |
|---|--|---|-----------------------------|----------------|
| Bibenzil (moles) | $\text{K}_2\text{Cr}_2\text{O}_7$ (moles) | $(\text{NH}_4)_2\text{Ce(NO}_3)_4$ (moles) | Reaction Conditions | Benzil (%) |
| 0.05 | 0.07 | 0.001 | 20 hrs. refluxing HOAc | 32 (51.5) |
| 0.05 | 0.11 | 0.001 | 20 hrs. refluxing HOAc | 31.4 (47.6) |
| 0.05 | 0.11 | 0.001 | 30 hrs. refluxing HOAc | 31.4 (47.6) |
| 0.05 | 0.22 | 0.002 | 20 hrs. refluxing HOAc | 30.7 (46.5) |
| 0.05 | 0.11 | 0.001 | 19 hrs. refluxing HOAc | 30.7 (46.5) |
| 0.05 | 0.11 | 0.001 | 19 hrs. room temperature | 0.0 |
| 0.05 | 0.22 | 0.001 | 43 hrs. refluxing HOAc | 40.0 (pure) |

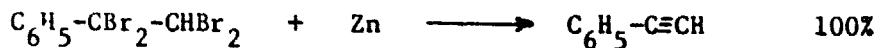
the starting material. To this end treatment of one omle of phenylacetylene with 1.3 moles of the oxidizing mixture was attempted and found to yield a 76% yield of benzoic acid.



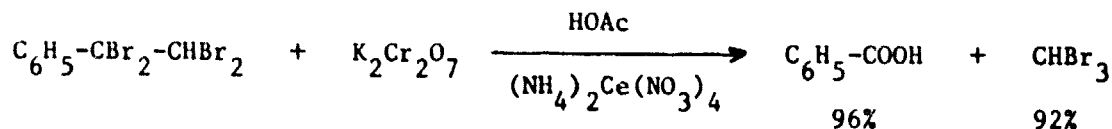
To prevent oxidative cleavage of the triple bond an attempt was made to protect it by converting it into the tetrabromide by reaction with excess bromine; a quantitative conversion was obtained. The triple bond



was then reintroduced into the molecule by reaction with zinc, the yield again being quantitative. However, when the tetrabromide was treated with



the oxidizing mixture, benzoic acid and bromoform were obtained in 96 and 92% yields, respectively.



Since this approach also had inherent difficulties associated with it, a new approach utilizing a coupling reaction of a protected copper acetylide with halobenzil will be investigated.

Experimental Section

Attempted Condensation of p,p'-Dibromobenzil and Potassium Acetylide in Liquid Ammonia. Into a 500 ml three-necked round-bottomed flask equipped with a dry-ice condenser was placed 300 ml of liquid ammonia and 0.5 g of ferric nitrate catalyst. Into this stirred solution was placed slowly 5.1 g (0.13 moles) of potassium in small pieces. The solution first turned a deep blue then grey, and then acetylene was introduced through a gas dispersion tube at 5 psi gauge pressure for 1000 sec. At this point 3.68 g (0.01 moles) of p,p'-dibromobenzil was introduced as a solid all at once and the reaction mixture stirred for 14 hrs. After this time the liquid ammonia was allowed to evaporate and the residue quenched with 200 ml of ice-water and extracted three times with 200 ml portions of ether. The ether extracts were combined, dried over magnesium sulfate and evaporated to afford a red oil, which was dissolved in 200 ml of hot benzene. Upon cooling 0.93 g (0.005 moles, 50%) of p-bromobenzamide, mp 191-192°, precipitated as a white crystalline solid. Chromatography of the remaining benzene solution afforded 0.63 g (0.003 moles, 30%) of 3-(p-bromophenyl)-3-hydroxypropyne, mp 30°, ir alcohol OH at 3610 cm^{-1} and C C-H at 3660 cm^{-1} . Also obtained was 10% of a yellow oil which showed a carbonyl peak in the ir at 1650 cm^{-1} and a halide in the Beilstein test, however this material could not be crystallized or identified further.

A sample of 3-(p-bromophenyl)-3-hydroxypropyne was submitted for analysis.

Anal. Calcd for $\text{C}_9\text{H}_7\text{OBr}$: C, 51.21; H, 3.34; Br, 37.86.

Found : C, 51.44; H, 3.26; Br, 37.52.

Attempted Condensation of p,p'-Dibromobenzil and Potassium Acetylide in Toluene. Into a 50 ml three-necked round-bottomed flask equipped with a condenser and a mechanical stirrer was placed 1.75 g (0.04 moles) of potassium in 10 ml of dry toluene and the mixture heated to 105-110°. At this point the potassium became molten and stirring was continued for several minutes. The stirring was then stopped and the mixture allowed to cool to room temperature at which point 25 ml of dry tetrahydrofuran (THF) was added to the suspension. Acetylene was then bubbled into the mixture slowly as previously described, whereupon the temperature in the flask rose to 40-50°. After the acetylene had been added, 3.58 g (0.01 moles) of p,p'-dibromobenzil was added as a solid all at once and the reaction mixture stirred for 14 hrs at 50°. After this time the reaction mixture was cooled, 200 ml of ice-water was added, the toluene layer removed and dried over anhydrous magnesium sulfate. Evaporation of the toluene afforded a red oil which was treated as previously described to afford 1.58 g (0.0075 moles, 75%) of 3-(p-bromophenyl)-3-hydroxypropyne and 15% of the same yellow oil obtained above.

Attempted Preparation of Potassium Acetylide in Toluene. To a refluxing solution of 50 ml of toluene, stirred by means of a high speed stirrer, was added small pieces of potassium until 2.0 g had been added. During the addition an explosion resulted which demolished the reaction flask and sprayed hot toluene and potassium into the hood. The resulting fire was extinguished with no serious effects.

4-Phenylacetylphenyl Ether (VI).⁵ To a stirred mixture of 58.7 g (0.44 mole) of anhydrous aluminum chloride and 150 ml of carbon disulfide cooled by means of an ice bath, was added a mixture of 68.2 g (0.44 mole) of phenylacetyl chloride and 33.0 g (0.194 mole) of phenyl ether over a period of 1 hr. After cooling and pouring onto a mixture of 200 g of ice and 100 g of concentrated hydrochloric acid, the dark red solution changed to a pale yellow-green product. The solid mass was filtered and washed with 2% hydrochloric acid, once with 5% sodium hydroxide solution, once with water, pressed and dried. The yellow-green product was recrystallized from 1 liter of benzene-alcohol (9:1) to give 57.0 g of silky, yellow needles, mp. 165-169°. A second crop (13.0 g) from the mother liquor also melted at 165-169°. Final recrystallization of the combined fractions from 700 ml of benzene gave 59.5 g (0.14 mole, 77%) of colorless, plate-like crystals, mp. 169-170° (Lit⁵ 169-170°).

4-(p-Acetylphenyl)acetylphenyl Ether (VII). Into a 500 ml three-necked round-bottomed flask, equipped with a mechanical stirrer, a reflux condenser and a dropping funnel was added 20.0 g (0.15 mole) of anhydrous aluminum chloride and 20.3 g (0.05 mole) of 4-phenylacetylphenyl ether (VI) in 100 ml of methylene chloride and the mixture stirred and cooled by means of an ice bath. Through the dropping funnel was added slowly 11.7 g (0.15 mole) of acetyl chloride and after the addition was completed the reaction mixture was stirred at room temperature for 1 hr and refluxed until all the hydrogen chloride was evolved, approximately 7.5 hrs. During this time the reaction mixture turned from light red to dark red to black, and after cooling the reaction mixture it was poured over 100 g of ice and 50 g of hydrochloric acid. The black reaction mixture turned a deep red

and the mixture was allowed to stand overnight to hydrolyze. Evaporation of the methylene chloride from the separated organic phase afforded a yellow-green solid which was filtered, washed with 2% hydrochloric acid solution, 5% sodium hydroxide solution then several times with water, pressed and dried to give 11.7 g of a yellowish product. The first recrystallization from ethanol gave a deep yellow solid, mp 136-137°, while a second recrystallization from ethanol gave a cream colored solid mp 139-140°. Overall yield 19.1 g (0.039 moles, 78%).

Anal. Calcd for $C_{32}H_{26}O_5$: C, 78.35; H, 5.34; O, 16.31.

Found : C, 78.21; H, 5.44.

4-Phenylacetyl-4'-Acetylphenylacetylphenyl Ether (X).- Using the same procedure as above except that 20.0 g (0.15 moles) of anhydrous aluminum chloride, 20.3 g (0.05 mole) of 4-phenylacetylphenyl ether (VI) and only 4.0 g (0.05 mole) of acetyl chloride was used, afforded 11.7 g (0.026 moles, 52%) of cream colored solid, mp 126-127° which nmr investigation proved to be the monoacetylated product.

Anal. Calcd for $C_{30}H_{24}O_4$: C, 80.34; H, 5.39; O, 14.27.

Found : C, 80.26; H, 5.42.

Reaction of VI with Vilsmeier Reagent. Preparation of 4-(β-chlorocinnamaldehyde)phenyl Ether. Into a 250 ml three-necked, round-bottomed-flask equipped with a reflux condenser, a mechanical stirrer and a dropping funnel was added 19.2 g (11.5 ml, 0.125 mole) of phosphorousoxy chloride ($POCl_3$) and 9.48 g (10.05 ml, 0.130 mole) of dimethylformamide (DMF). To this mixture was added slowly and dropwise 5.2 g (0.0128 mole) of 4-phenylacetylphenyl ether (VI) dissolved in 90 ml of DMF. The reaction

mixture turned red and was heated to 55-60° for 3 hrs, at which point the reaction mixture was dark red in color. Neutralization with a saturated solution of 50 g of sodium acetate in 120 ml of water afforded a yellow solid weighing 6.34 g. Recrystallization from a 4:1 benzene-hexane mixture afforded 6.2 g (0.0127 mole, 99.4%) of a cream colored solid, mp 184-185° which nmr showed to be the 4-(8-chlorocinnamaldehyde)phenyl ether.

Anal. Calcd for $C_{30}H_{20}O_2Cl_2$: C, 74.54; H, 4.17; O, 6.62; Cl, 14.67.

Found : C, 74.61; H, 4.10.

Reaction of VII with Vilsmeier Reagent (Scheme 3). Using the procedure reported above a Vilsmeier reaction was performed using 1 mole of VII to 3 moles of Vilsmeier reagent. To 9.36 g (5.6 ml, 0.0612 mole) of $POCl_3$ and 5.95 g (6.31 ml, 0.0816 mole) of DMF was added 10.0 g (0.0204 mole) of VII dissolved in 100 ml of DMF. Work-up as above afforded 11.25 g of crude solid mp 80-82°. Recrystallization from ethanol afforded 10.7 g (0.017 mole, 83.6%) of white solid, mp 84-85° which nmr showed to have only one unreacted methylene function. Starting material (VII) was also recovered.

Anal. Calcd for $C_{35}H_{23}Cl_3O_5$: C, 66.75; H, 3.66; Cl, 16.89; O, 12.70.

Found : C, 66.68; H, 3.49; Cl, 16.92.

Using the same procedure reported above and a 1:5 molar ratio of VII to Vilsmeier reagent afforded 10.9 g (0.0173 moles, 85%) of the same product.

Reaction of X with Vilsmeier Reagent (Scheme 4). Using the above procedure a 1:3 molar ratio of X to Vilsmeier reagent reaction was performed. To 5.139 g (3.07 ml, 0.0336 mole) of $POCl_3$ and 2.55 g (2.7 ml, 0.0350 mole)

of DMF was added 5.0 g (0.0112 mole) of monoacetyl product X dissolved in 45 ml of DMF. Work-up as above afforded 3.03 g (0.0056 mole, 50%) of yellow solid, mp 90-91°, which nmr showed to contain only one unreacted methylene function. Starting material (X) was also recovered.

Anal. Calcd for $C_{32}H_{22}Cl_2O_4$: C, 70.99; H, 4.10; Cl, 13.10; O, 11.81.

Found : C, 71.02; H, 4.13; Cl, 13.20.

Using the same procedure reported above and a 1:1.2 molar ratio of X to Villsmeier reagent afforded 0.6 g (0.00112 mole, 10%) of the same product.

Oxidation of Bibenzil. Preparation of Benzil. Into a 250 ml three-necked, round-bottomed flask equipped with a mechanical stirrer and a dropping funnel was placed 9.1 g (0.05 mole) of bibenzil, 0.5 g of ceric ammonium nitrate and 32.5 g (0.11 mole) of potassium dichromate all dissolved in 100 ml of glacial acetic acid. This reaction mixture was placed on a water bath and the temperature maintained at 38-43° for 2.5 hrs, after which time it was refluxed for 20 hrs. During this time the mixture turned a deep green color. After refluxing the mixture was poured into 300 ml of water and the solid which precipitated was digested for 0.5 hrs. at 80° on the water bath with 20 g of sodium carbonate dissolved in 400 ml of water. The solution was then extracted with 300 ml of hot benzene and allowed to cool giving a gelatin mixture which was filtered on a funnel packed with Celite. The benzene layer was separated, washed with water, dried over anhydrous magnesium sulfate and evaporated. The residue was taken up in alcohol and fractional crystallization afforded benzil. A mixture melting point with a commercial sample showed no depression.

Various reaction conditions and ratios of reagents were used in an attempt to increase the yield of benzil, the results of this study are reported in Table I.

Reaction of Phenylacetylene with Oxidizing Agent. Into a 250 ml one-necked round-bottomed-flask equipped with a reflux condenser was placed 5.1 g (0.05 mole) of phenylacetylene, 20.6 g (0.07 mole) of potassium dichromate, 0.5 g of ceric ammonium nitrate and 100 ml of acetic acid and the mixture refluxed for 21 hrs. This produced a dark green reaction mixture which was worked up as above using ether as the extraction solvent and afforded 4.2 g (0.034 mole, 76%) of benzoic acid, mp 120-121°. A mixture melting point with a commercial sample showed no depression.

Reaction of Phenylacetylene With Bromine. Into a 100 ml one-necked round-bottomed-flask equipped with a reflux condenser was placed 11.0 g (0.15 mole) of bromine in 30 ml of carbon tetrachloride and 5.0 g (0.05 mole) of phenylacetylene dissolved in 30 ml of carbon tetrachloride was added slowly. After the addition was completed, the reaction mixture was refluxed for 20 hrs., cooled and the carbon tetrachloride and excess bromine were removed on the rotoevaporator. This afforded 21.8 g (0.05 mole, 100%) of white 1,1,2,2-tetrabromoethylbenzene.

Reaction of 1,1,2,2-Tetrabromoethylbenzene with Zinc. Into a 100 ml, one-necked, round-bottomed-flask equipped with a magnetic stirrer and a reflux condenser was placed 4.21 g (0.01 mole) of 1,1,2,2 -tetrabromoethylbenzene, 1.0 g (0.015 mole) of 20 mesh zinc and 50 ml of benzene and the mixture heated to reflux. After 20 hrs the solid zinc bromide was filtered and

the benzene evaporated affording a liquid which upon distillation afforded 1.02 g (0.01 mole, 100%) of phenylacetylene.

Reaction of 1,1,2,2-Tetrabromoethylbenzene with Oxidizing Agent. Into a 250 ml, one-necked, round-bottomed-flask was placed 20.0 g (0.05 mole) of 1,1,2,2-tetrabromoethylbenzene, 20.6 g (0.07 mole) of potassium dichromate, 0.5 g of ceric ammonium nitrate and 100 ml of acetic acid, and the mixture refluxed for 21 hrs. After 0.5 hrs of heating the solution turned a dark red color. After refluxing 21 hrs, the solution was quenched by pouring it onto 400 ml of water, filtered and the filtrate extracted with ether. The ether was dried and evaporated to afford 5.86 g (0.048 mole, 96%) of benzoic acid, mp 122°. The aqueous layer had a very strong characteristic odor of bromoform and upon fractional distillation 11.6 g (0.046 mole, 92%) of bromoform was found to distill at 146°.

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